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(54) Title: A PROCESS FOR MAKING POLYOLEFINS HAVING BROAD MOLECULAR WEIGHT DISTRIBUTIONS

(57) Abstract

A process for producing polyolefin resins with a broad molecular weight distribution comprising reacting one or more olefins in the presence of a reduced transition metal complex and a co-catalyst. The transition metal complex consists of a reduced transition metal, chosen from groups 4-6 of the Periodic Table of the Elements, with a multidentate monoanionic ligand and with two monoanionic ligands. In particular the reduced transition metal is preferably titanium (Ti).

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5                    A PROCESS FOR MAKING POLYOLEFINS HAVING  
                    BROAD MOLECULAR WEIGHT DISTRIBUTIONS

BACKGROUND TO THE INVENTION

10    1.            Field of the Invention

                    The present invention relates to a process  
                    for preparing a polyolefin having a broad molecular  
                    weight distribution with use of a catalyst system  
                    comprising a transition metal complex and a co-  
15    catalyst.

                    2.            Description of Related Art

                    Polyolefins are needed which have a broad  
                    molecular weight distribution (MWD) and good processing  
20    behavior. The term "broad molecular weight  
                    distribution" when used in relation to the present  
                    polyolefins, means a multimodal or at least bimodal, or  
                    even broad monomodal molecular weight distribution (MWD  
                    =  $M_w/M_n$  above 3.5).

25                    A process for producing polyolefins with  
                    broad MWD is disclosed in, for example, EP-A-619325.  
                    This reference describes contacting at least one olefin  
                    under polymerization conditions with a supported  
                    catalyst system. The catalyst system comprises an  
30    aluminoxane and at least two metallocenes containing  
                    the same transition metal, selected from mono, di and  
                    tri-cyclopentadienyls and substituted cyclopentadienyls  
                    of a transition metal. At least one of the  
                    metallocenes is bridged and at least one of the  
35    metallocenes is unbridged.

                    A disadvantage of the use of two or more  
                    metallocene compounds combined, either supported or  
                    unsupported, is the possibility of side reactions like  
                    ligand exchange reactions or the formation of dimers

without activity or with a low activity. A further disadvantage is also that in such a process at least two reaction steps are required for the synthesis of the two metallocenes. As soon as one or both  
5 metallocene components have to be supported on a support material, even more reaction steps are required.

The purpose of the present invention is to provide a process for preparing polyolefin resins with  
10 a broad molecular weight distribution, using a transition metal complex catalyst and a co-catalyst, which avoids the drawbacks of the known processes. A further purpose of this invention is to provide such a process in which the broad MWD can be obtained in  
15 either solution, bulk, slurry or gas phase polymerization processes, and in which the bimodality or multimodality and/or width of the MWD can be influenced by, for instance, the type of cocatalyst used, the temperature, the comonomer, the catalyst  
20 support, and the like.

Presently, commercial samples of HDPE with a bimodal MWD are produced in a tandem reactor process wherein two reactors are run in series. The catalyst is exposed to ethylene polymerization conditions in one  
25 reactor, and the resulting polymer-catalyst particles are transferred to a second reactor for additional polymerization. In the two reactors, the amount of hydrogen is different. Relatively lower molecular weight product is produced in the reactor containing  
30 more hydrogen, because the hydrogen acts as a chain transfer agent, and relatively higher molecular weight product is produced in the reactor containing lower proportions of hydrogen.

The disadvantage of the process described  
35 above is obvious. For the tandem reactor process, (at least) two reactors are required which implies high

capital expenditure.

Polyolefin blends of bimodal MWD are disclosed in WO 95/11264 which describes HDPE resin blends of broad bimodal molecular weight distribution, catalytically produced in situ. The resins are produced by a catalyst obtained by supporting a MAO-activated n-butyl-zirconocene on a conventional Ziegler-Natta catalyst:  $\text{Ti/MgCl}_2/\text{SiO}_2$ .

Another process is disclosed in EP-A-447 070 where zirconocenes were combined with a conventional  $\text{MgCl}_2$ -based Ziegler-Natta catalyst system.

In all these references, the metal center of the metallocene catalyst is in its highest formal oxidation state. Further examples of such metallocene catalyst systems are disclosed in Polymer 35 (4), 1994, p. 808, in DE-A-3825814 and in WO-A-95/30698.

The combination of a metallocene catalyst with a conventional Ziegler-Natta catalyst involves a multistep catalyst synthesis. First, the Ziegler-Natta catalyst has to be synthesized. In a further reaction step, the metallocene has to be combined with this Ziegler-Natta catalyst. A further disadvantage of such a system is that the cocatalyst for the activation of one part of such a system, for example the Ziegler-Natta part, is most often not able to activate the other component, e.g. the metallocene, or can even deactivate the other component. An even further disadvantage of the mentioned system is that compounds usually used to regulate the structure of the polyolefin produced by Ziegler-Natta catalyst systems, so called donor compounds, can have a detrimental effect on the working of the metallocene-part of the catalyst system.

An important disadvantage of many of the known catalyst systems described above is indeed that they only produce polymers with a bimodal or broad MWD

under specific polymerization conditions. Examples include a very narrow polymerization temperature range, very dry condition, and/or specific catalyst/monomer combinations.

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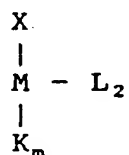
### SUMMARY OF THE INVENTION

Broad molecular weight distributions can be achieved by the use of particular transition metal complexes in the catalyst system.

10

The catalyst composition includes at least one complex comprising a reduced valency transition metal (M) selected from groups 4-6 of the Periodic Table of Elements, a multidentate monoanionic ligand (X), two monoanionic ligands (L), and, optionally, additional ligands (K). More specifically, the complex of the catalyst composition of the present invention is represented by the following formula (I):

20



(I)

25

wherein the symbols have the following meanings:

- M a reduced transition metal selected from group 4, 5 or 6 of the Periodic Table of Elements;
- 30 X a multidentate monoanionic ligand represented by the formula:  $(Ar-R_t-)_s Y(-R_t-DR'_n)_q$ ;
- Y a cyclopentadienyl, amido  $(-NR'-)$ , or phosphido group  $(-PR'-)$ , which is bonded to the reduced transition metal M;
- 35 R at least one member selected from the group consisting of (i) a connecting group between the Y group and the  $DR'_n$  group and (ii) a connecting group between the Y group and the Ar group,

- wherein when the ligand X contains more than one R group, the R groups can be identical to or different from each other;
- D an electron-donating hetero atom selected from group 15 or 16 of the Periodic Table of Elements;
- R' a substituent selected from the group consisting of a hydrogen, hydrocarbon radical and hetero atom-containing moiety, except that R' cannot be hydrogen when R' is directly bonded to the electron-donating hetero atom D, wherein when the multidentate monoanionic ligand X contains more than one substituent R', the substituents R' can be identical or different from each other;
- Ar an electron-donating aryl group;
- L a monoanionic ligand bonded to the reduced transition metal M, wherein the monoanionic ligand L is not a ligand comprising a cyclopentadienyl, amido (-NR'-), or phosphido (-PR'-) group, and wherein the monoanionic ligands L can be identical or different from each other;
- K a neutral or anionic ligand bonded to the reduced transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or different from each other;
- m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for  $M^{3+}$ , m is 1 for  $M^{4+}$ , and m is 2 for  $M^{5+}$ , and when K is a neutral ligand m increases by one for each neutral K ligand;
- n the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from group 16 of the Periodic Table of Elements n is 1;
- q,s q and s are the number of  $(-R_t-DR'_n)$  groups and

(Ar-R<sub>t</sub>-) groups bonded to group Y, respectively, wherein q + s is an integer not less than 1; and the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and DR'<sub>n</sub> groups, wherein t is selected independently as 0 or 1.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate the present invention. In such drawings:

FIG. 1 is a schematic view of a cationic active site of a trivalent catalyst complex in accordance with an embodiment of the present invention; and

FIG. 2 is a schematic view of a neutral active site of a trivalent catalyst complex of a dianionic ligand of a conventional catalyst complex according to WO-A-93/19104.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Various components (groups) of the transition metal complex are discussed below in more detail.

##### (a) The Transition Metal (M)

The transition metal in the complex is selected from groups 4-6 of the Periodic Table of Elements. As referred to herein, all references to the Periodic Table of Elements mean the version set forth in the new IUPAC notation found on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990, the complete disclosure of which is incorporated herein by reference. More preferably, the transition metal is selected from group 4 of the Periodic Table of Elements, and most preferably is titanium (Ti).

The transition metal is present in reduced form in the complex, which means that the transition



metal is in a reduced oxidation state. As referred to herein, "reduced oxidation state" means an oxidation state which is greater than zero but lower than the highest possible oxidation state of the metal (for example, the reduced oxidation state is at most  $M^{3+}$  for a transition metal of group 4, at most  $M^{4+}$  for a transition metal of group 5 and at most  $M^{5+}$  for a transition metal of group 6).

10 (b) The X Ligand

The X ligand is a multidentate monoanionic ligand represented by the formula:  $(Ar-R_t-)_s Y(-R_t-DR'_n)_q$ .

As referred to herein, a multidentate monoanionic ligand is bonded with a covalent bond to the reduced transition metal (M) at one site (the anionic site, Y) and is bonded either (i) with a coordinate bond to the transition metal at one other site (bidentate) or (ii) with a plurality of coordinate bonds at several other sites (tridentate, tetradentate, etc.). Such coordinate bonding can take place, for example, via the D heteroatom or Ar group(s). Examples of tridentate monoanionic ligands include, without limitation,  $Y-R_t-DR'_{n-1}-R_t-DR'_n$  and  $Y(-R-DR'_n)_2$ . It is noted, however, that heteroatom(s) or aryl substituent(s) can be present on the Y group without coordinately bonding to the reduced transition metal M, so long as at least one coordinate bond is formed between an electron-donating group D or an electron donating Ar group and the reduced transition metal M.

R represents a connecting or bridging group between the  $DR'_n$  and Y, and/or between the electron-donating aryl (Ar) group and Y. Since R is optional, "t" can be zero. The R group is discussed below in paragraph (d) in more detail.

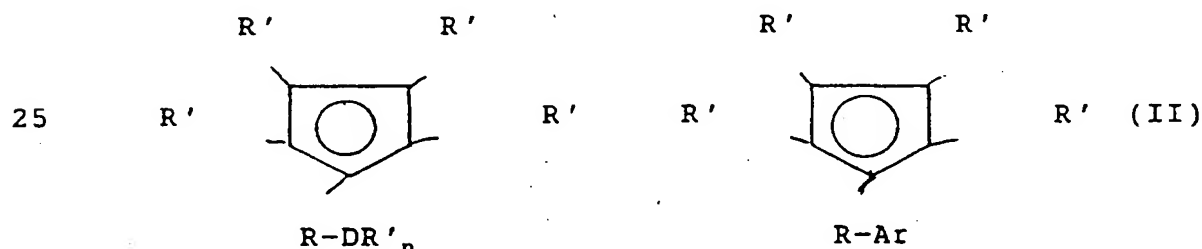
## (c) The Y Group

The Y group of the multidentate monoanionic ligand (X) is preferably a cyclopentadienyl, amido ( $-\text{NR}'-$ ), or phosphido ( $-\text{PR}'-$ ) group.

Most preferably, the Y group is a cyclopentadienyl ligand (Cp group). As referred to herein, the term cyclopentadienyl group encompasses substituted cyclopentadienyl groups such as indenyl, fluorenyl, and benzoindenyl groups, and other polycyclic aromatics containing at least one 5-member diene ring, so long as at least one of the substituents of the Cp group is an  $\text{R}_t\text{-DR}'_n$  group or  $\text{R}_t\text{-Ar}$  group that replaces one of the hydrogens bonded to the five-member ring of the Cp group via an exocyclic substitution.

Examples of a multidentate monoanionic ligand with a Cp group as the Y group (or ligand) include the following (with the ( $-\text{R}_t\text{-DR}'_n$ ) or ( $\text{Ar-R}_t-$ ) substituent on the ring):

20

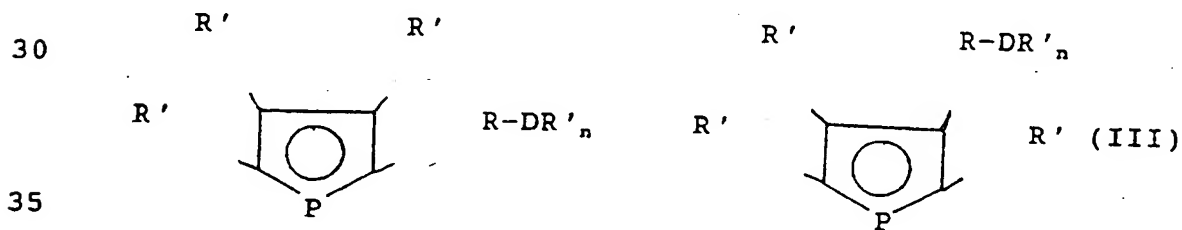


The Y group can also be a hetero cyclopentadienyl group. As referred to herein, a hetero cyclopentadienyl group means a hetero ligand derived from a cyclopentadienyl group, but in which at least one of the atoms defining the five-member ring structure of the cyclopentadienyl is replaced with a hetero atom via an endocyclic substitution. The hetero Cp group also includes at least one  $\text{R}_t\text{-DR}'_n$  group or

$R_t$ -Ar group that replaces one of the hydrogens bonded to the five-member ring of the Cp group via an exocyclic substitution. As with the Cp group, as referred to herein the hetero Cp group encompasses indenyl, fluorenyl, and benzoindenyl groups, and other polycyclic aromatics containing at least one 5-member dienyli ring, so long as at least one of the substituents of the hetero Cp group is an  $R_t$ -DR'<sub>n</sub> group or  $R_t$ -Ar group that replaces one of the hydrogens bonded to the five-member ring of the hetero Cp group via an exocyclic substitution.

The hetero atom can be selected from group 14, 15 or 16 of the Periodic Table of Elements. If there is more than one hetero atom present in the five-member ring, these hetero atoms can be either the same or different from each other. More preferably, the hetero atom(s) is/are selected from group 15, and still more preferably the hetero atom(s) selected is/are phosphorus.

By way of illustration and without limitation, representative hetero ligands of the X group that can be practiced in accordance with the present invention are hetero cyclopentadienyl groups having the following structures, in which the hetero cyclopentadienyl contains one phosphorus atom (i.e., the hetero atom) substituted in the five-member ring:



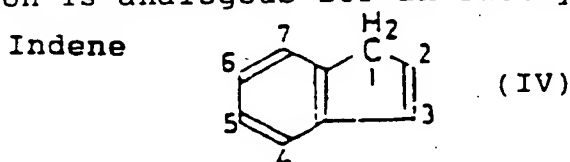
40

It is noted that, generally, the transition

metal group M is bonded to the Cp group via an  $\eta^5$  bond.

The other R' exocyclic substituents (shown in formula (III)) on the ring of the hetero Cp group can be of the same type as those present on the Cp group, as represented in formula (II). As in formula (II), at least one of the exocyclic substituents on the five-member ring of the hetero cyclopentadienyl group of formula (III) is the  $R_t-DR'_n$  group or the  $R_t-Ar$  group.

10           The numeration of the substitution sites of  
the indenyl group is in general and in the present  
description based on the IUPAC Nomenclature of Organic  
Chemistry 1979, rule A 21.1. The numeration of the  
substituent sites for indene is shown below. This  
15 numeration is analogous for an indenyl group:



20 The Y group can also be an amido ( $-NR'-$ ) group or a phosphido ( $-PR'-$ ) group. In these alternative embodiments, the Y group contains nitrogen (N) or phosphorus (P) and is bonded covalently to the transition metal M as well as to the (optional) R group  
25 of the ( $-R_t-DR'_n$ ) or ( $Ar-R_t-$ ) substituent.

(d)            The R Group

The R group is optional, such that it can be absent from the X group. Where the R group is absent, the DR'<sub>n</sub> or Ar group is bonded directly to the Y group (that is, the DR'<sub>n</sub> or Ar group is bonded directly to the Cp, amido, or phosphido group). The presence or absence of an R group between each of the DR'<sub>n</sub> groups and/or Ar groups is independent.

Where at least one of the R groups is present; each of the R group constitutes the connecting bond between, on the one hand the Y group, and on the

other hand the  $DR'_n$  group or the Ar group. The presence and size of the R group determines the accessibility of the transition metal M relative to the  $DR'_n$  or Ar group, which gives the desired intramolecular coordination. If the R group (or bridge) is too short or absent, the donor may not coordinate well due to ring tension. The R groups are each selected independently, and can generally be, for example, a hydrocarbon group with 1-20 carbon atoms (e.g., alkylidene, arylidene, aryl alkylidene, etc.). Specific examples of such R groups include, without limitation, methylene, ethylene, propylene, butylene, phenylene, whether or not with a substituted side chain. Preferably, the R group has the following structure:



where  $p = 1-4$ . The  $R'$  groups of formula (IV) can each be selected independently, and can be the same as the  $R'$  groups defined below in paragraph (g).

In addition to carbon, the main chain of the R group can also contain silicon or germanium. Examples of such R groups are: dialkyl silylene ( $-SiR'_2-$ ), dialkyl germylene ( $-GeR'_2-$ ), tetra-alkyl silylene ( $-SiR'_2-SiR'_2-$ ), or tetraalkyl silaethylene ( $-SiR'_2CR'_2-$ ). The alkyl groups in such a group preferably have 1-4 carbon atoms and more preferably are a methyl or ethyl group.

### 30 (e) The $DR'_n$ Group

This donor group consists of an electron-donating hetero atom D, selected from group 15 or 16 of the Periodic Table of Elements, and one or more substituents  $R'$  bonded to D. The number (n) of  $R'$  groups is determined by the nature of the hetero atom D, insofar as n being 2 if D is selected from group 15

and n being 1 if D is selected from group 16. The R' substituents bonded to D can each be selected independently, and can be the same as the R' groups defined below in paragraph (g), with the exception that  
5 the R' substituent bonded to D cannot be hydrogen.

The hetero atom D is preferably selected from the group consisting of nitrogen (N), oxygen (O), phosphorus (P) and sulphur (S); more preferably, the hetero atom is nitrogen (N). Preferably, the R' group  
10 is an alkyl, more preferably an n-alkyl group having 1-20 carbon atoms, and most preferably an n-alkyl having 1-8 carbon atoms. It is further possible for two R' groups in the DR'<sub>n</sub> group to be connected with each other to form a ring-shaped structure (so that the DR'<sub>n</sub>  
15 group can be, for example, a pyrrolidinyl group). The DR'<sub>n</sub> group can form coordinate bonds with the transition metal M.

(f) The Ar Group

20 The electron-donating group (or donor) selected can also be an aryl group (C<sub>6</sub>R'<sub>5</sub>), such as phenyl, tolyl, xylyl, mesityl, cumenyl, tetramethyl phenyl, pentamethyl phenyl, a polycyclic group such as triphenylmethane, etc. The electron-donating group D of  
25 formula (I) cannot, however, be a substituted Cp group, such as an indenyl, benzoindenyl, or fluorenyl group.

The coordination of this Ar group in relation to the transition metal M can vary from  $\eta^1$  to  $\eta^6$ .

30 (g) The R' Group

The R' groups may each separately be hydrogen or a hydrocarbon radical with 1-20 carbon atoms (e.g. alkyl, aryl, aryl alkyl and the like as shown in Table  
1).

35 Examples of alkyl groups are methyl, ethyl, propyl, butyl, hexyl and decyl. Examples of aryl groups are

phenyl, mesityl, tolyl and cumenyl. Examples of aryl alkyl groups are benzyl, pentamethylbenzyl, xylyl, styryl and trityl. Examples of other R' groups are halides, such as chloride, bromide, fluoride and iodide, methoxy, ethoxy and phenoxy.

Also, two adjacent hydrocarbon radicals of the Y group can be connected with each other to define a ring system; therefore the Y group can be an indenyl, a fluorenyl or a benzoindenyl group. The indenyl, fluorenyl, and/or benzoindenyl can contain one or more R' groups as substituents. R' can also be a substituent which instead of or in addition to carbon and/or hydrogen can comprise one or more hetero atoms of groups 14-16 of the Periodic Table of Elements. Thus, a substituent can be, for example, a Si-containing group, such as  $\text{Si}(\text{CH}_3)_3$ .

(h) The L Group

The transition metal complex contains two monoanionic ligands L bonded to the transition metal M. Examples of the L group ligands, which can be identical or different, include, without limitation, the following: a hydrogen atom; a halogen atom; an alkyl, aryl or aryl alkyl group; an alkoxy or aryloxy group; a group comprising a hetero atom selected from group 15 or 16 of the Periodic Table of Elements, including, by way of example, (i) a sulphur compound, such as sulphite, sulphate, thiol, sulphonate, and thioalkyl, and (ii) a phosphorus compound, such as phosphite, and phosphate. The two L groups can also be connected with each other to form a dianionic bidentate ring system.

These and other ligands can be tested for their suitability by means of simple experiments by one skilled in the art.

Preferably, L is a halide and/or an alkyl or aryl group; more preferably, L is a Cl group and/or a

C<sub>1</sub>-C<sub>4</sub> alkyl or a benzyl group. The L group, however, cannot be a Cp, amido, or phosphido group. In other words, L cannot be one of the Y groups.

5 (i) The K Ligand

The K ligand is a neutral or anionic group bonded to the transition metal M. The K group is a neutral or anionic ligand bonded to M. When K is a neutral ligand K may be absent, but when K is  
10 monoanionic, the following holds for K<sub>m</sub>:

m = 0 for M<sup>3+</sup>

m = 1 for M<sup>4+</sup>

m = 2 for M<sup>5+</sup>

On the other hand, neutral K ligands, which  
15 by definition are not anionic, are not subject to the same rule. Therefore, for each neutral K ligand, the value of m (i.e., the number of total K ligands) is one higher than the value stated above for a complex having all monoanionic K ligands.

20 The K ligand can be a ligand as described above for the L group or a Cp group (-C<sub>5</sub>R'<sub>5</sub>), an amido group (-NR'<sub>2</sub>) or a phosphido group (-PR'<sub>2</sub>). The K group can also be a neutral ligand such as an ether, an amine, a phosphine, a thioether, among others.

25 If two K groups are present, the two K groups can be connected with each other via an R group to form a bidentate ring system.

As can also be seen from formula (I), the X group of the complex contains a Y group to which are  
30 linked one or more donor groups (the Ar group(s) and/or DR'<sub>n</sub> group(s)) via, optionally, an R group. The number of donor groups linked to the Y group is at least one and at most the number of substitution sites present on a Y group.

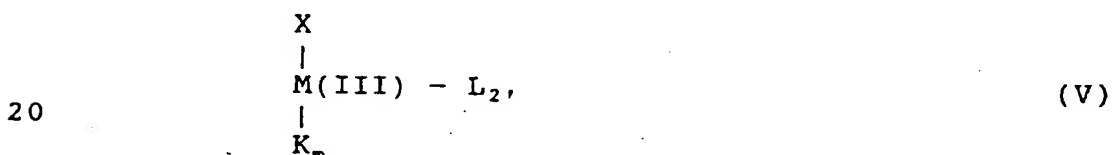
35 With reference, by way of example, to the structure according to formula (II), at least one



substitution site on a Cp group is made by an  $R_t$ -Ar group or by an  $R_t$ -DR'<sub>n</sub> group (in which case  $q + s = 1$ ). If all the R' groups in formula (II) were  $R_t$ -Ar groups,  $R_t$ -DR'<sub>n</sub> groups, or any combination thereof, the value of  
 5 (q + s) would be 5.

One preferred embodiment of the catalyst composition according to the present invention comprises a transition metal complex in which a bidentate/monoanionic ligand is present and in which  
 10 the reduced transition metal has been selected from group 4 of the Periodic Table of Elements and has an oxidation state of +3.

In this case, the catalyst composition according to the invention comprises a transition metal  
 15 complex represented by formula (V):



where the symbols have the same meaning as described above for formula (I) and where M(III) is a transition  
 25 metal selected from group 4 of the Periodic Table of Elements and is in oxidation state 3+.

Such a transition metal complex has no anionic K ligands (for an anionic K,  $m = 0$  in case of  $M^{3+}$ ).

30 It should be pointed out that in WO-A-93/19104, transition metal complexes are described in which a group 4 transition metal in a reduced oxidation state (3+) is present. The complexes described in WO-A-93/19104 have the general formula:



The Y group in this formula (VI) is a hetero atom, such

as phosphorus, oxygen, sulfur, or nitrogen bonded covalently to the transition metal M (see p. 2 of WO-A-93/19104). This means that the  $\text{Cp}_a(\text{ZY})_b$  group is of a dianionic nature, and has the anionic charges residing  
5 formerly on the Cp and Y groups. Accordingly, the  $\text{Cp}_a(\text{ZY})_b$  group of formula (VI) contains two covalent bonds: the first being between the 5-member ring of the Cp group and the transition metal M, and the second being between the Y group and the transition metal. By  
10 contrast, the X group in the complex according to the present invention is of a monoanionic nature, such that a covalent bond is present between the Y group (e.g., the Cp group) and transition metal, and a coordinate bond can be present between the transition metal M and  
15 one or more of the  $(\text{Ar}-\text{R}_t-)$  and  $(-\text{R}_t-\text{DR}'_n)$  groups. This changes the nature of the transition metal complex and consequently the nature of the catalyst that is active in the polymerization. As referred to herein, a coordinate bond is a bond (e.g.,  $\text{H}_3\text{N}-\text{BH}_3$ ) which when  
20 broken, yields either (i) two species without net charge and without unpaired electrons (e.g.,  $\text{H}_3\text{N}:$  and  $\text{BH}_3$ ) or (ii) two species with net charge and with unpaired electrons (e.g.,  $\text{H}_3\text{N}^+$  and  $\text{BH}_3^-$ ). On the other hand, as referred to herein, a covalent bond is a bond  
25 (e.g.,  $\text{CH}_3-\text{CH}_3$ ) which when broken yields either (i) two species without net charge and with unpaired electrons (e.g.,  $\text{CH}_3\cdot$  and  $\text{CH}_3\cdot$ ) or (ii) two species with net charges and without unpaired electrons (e.g.,  $\text{CH}_3^+$  and  $\text{CH}_3^-$ ). A discussion of coordinate and covalent bonding  
30 is set forth in Haaland et al. (Angew. Chem Int. Ed. Eng. Vol. 28, 1989, p. 992), the complete disclosure of which is incorporated herein by reference.

The following explanation is proposed, although it is noted that the present invention is in  
35 no way limited to this theory.

Referring now more particularly to FIG. 2,

the transition metal complexes described in WO-A-93/19104 are ionic after interaction with the co-catalyst. However, the transition metal complex according to WO-A-93/19104 that is active in the polymerization contains an overall neutral charge (on the basis of the assumption that the polymerizing transition metal complex comprises, a M(III) transition metal, one dianionic ligand and one growing monoanionic polymer chain (POL)). By contrast, as shown in FIG. 1, the polymerization active transition metal complex of the catalyst composition according to the present invention is of a cationic nature (on the basis of the assumption that the polymerizing transition metal complex - based on the formula (V) structure - comprises, a M(III) transition metal, one monoanionic bidentate ligand and one growing monoanionic polymer chain (POL)).

Transition metal complexes in which the transition metal is in a reduced oxidation state, but have the following structure:



are generally not active in co-polymerization reactions. It is precisely the presence, in the transition metal complex of the present invention, of the DR', or Ar group (the donor), optionally bonded to the Y group by means of the R group, that gives a stable transition metal complex suitable for polymerization.

Such an intramolecular donor is to be preferred over an external (intermolecular) donor on account of the fact that the former shows a stronger and more stable coordination with the transition metal complex.

It will be appreciated that the catalyst

system may also be formed in situ if the components thereof are added directly to the polymerization reactor system and a solvent or diluent, including liquid monomer, is used in said polymerization reactor.

5           The catalyst composition of the present invention also contains a co-catalyst. For example, the co-catalyst can be an organometallic compound. The metal of the organometallic compound can be selected from group 1, 2, 12 or 13 of the Periodic Table of  
10 Elements. Suitable metals include, for example and without limitation, sodium, lithium, zinc, magnesium, and aluminum, with aluminum being preferred. At least one hydrocarbon radical is bonded directly to the metal to provide a carbon-metal bond. The hydrocarbon group  
15 used in such compounds preferably contains 1-30, more preferably 1-10 carbon atoms. Examples of suitable compounds include, without limitation, amyl sodium, butyl lithium, diethyl zinc, butyl magnesium chloride, and dibutyl magnesium. Preference is given to  
20 organoaluminium compounds, including, for example and without limitation, the following: trialkyl aluminum compounds, such as triethyl aluminum and tri-isobutyl aluminum; alkyl aluminum hydrides, such as di-isobutyl aluminum hydride; alkylalkoxy organoaluminium  
25 compounds; and halogen-containing organoaluminium compounds, such as diethyl aluminum chloride, diisobutyl aluminum chloride, and ethyl aluminum sesquichloride. Preferably, linear or cyclic aluminoxanes are selected as the organoaluminium  
30 compound.

          In addition or as an alternative to the organometallic compounds as the co-catalyst, the catalyst composition of the present invention can include a compound which contains or yields in a  
35 reaction with the transition metal complex of the present invention a non-coordinating or poorly

coordinating anion. Such compounds have been described for instance in EP-A-426,637, the complete disclosure of which is incorporated herein by reference. Such an anion is bonded sufficiently unstably such that it is replaced by an unsaturated monomer during the co-polymerization. Such compounds are also mentioned in EP-A-277,003 and EP-A-277,004, the complete disclosures of which are incorporated herein by reference. Such a compound preferably contains a triaryl borane or a tetraaryl borate or an aluminum equivalent thereof. Examples of suitable co-catalyst compounds include, without limitation, the following:

- dimethyl anilinium tetrakis (pentafluorophenyl) borate  $[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{H}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ ;
- 15 - dimethyl anilinium bis (7,8-dicarbaundecaborate)-cobaltate (III);
- tri(n-butyl)ammonium tetraphenyl borate;
- triphenylcarbenium tetrakis (pentafluorophenyl) borate;
- 20 - dimethylanilinium tetraphenyl borate;
- tris(pentafluorophenyl) borane; and
- tetrakis(pentafluorophenyl) borate.

If the above-mentioned non-coordinating or poorly coordinating anion is used, it is preferable for the transition metal complex to be alkylated (that is, the L group is an alkyl group). As described for instance in EP-A-500,944, the complete disclosure of which is incorporated herein by reference, the reaction product of a halogenated transition metal complex and an organometallic compound, such as for instance triethyl aluminum (TEA), can also be used.

The molar ratio of the co-catalyst relative to the transition metal complex, in case an organometallic compound is selected as the co-catalyst, usually is in a range of from about 1:1 to about 10,000:1, and preferably is in a range of from about

1:1 to about 2,500:1. If a compound containing or yielding a non-coordinating or poorly coordinating anion is selected as co-catalyst, the molar ratio usually is in a range of from about 1:100 to about 1,000:1, and preferably is in a range of from about 1:2 to about 250:1.

As a person skilled in the art would be aware, the transition metal complex as well as the co-catalyst can be present in the catalyst composition as a single component or as a mixture of several components. For instance, a mixture may be desired where there is a need to influence the molecular properties of the polymer, such as molecular weight and in particular molecular weight distribution.

The catalyst composition according to the invention can be used by a method known as such as a catalyst component for the polymerization of an olefin. The olefin can be, for example, an  $\alpha$ -olefin, an internal olefin, a cyclic olefin, a di-olefin, or mixtures thereof.

The invention relates in particular to a process for the polymerization of an  $\alpha$ -olefin. The  $\alpha$ -olefin preferably is ethylene, propylene, n-butene, n-pentene, n-hexene, n-heptene, n-octene, n-styrene and mixtures thereof. More preferably, ethylene and/or propylene, ethylene and/or octene, or ethylene and/or styrene are used as  $\alpha$ -olefin.

The use of such olefins results in the formation of (semi)crystalline polyethylene homo- and co-polymers, of high or low density (HDPE, LDPE, LLDPE, Ethylene/Styrene copolymers, etc.), and polypropylene, homo- and copolymers (PP and EMPP). The monomers needed for such products and the polymerization processes to be used are known to the person skilled in the art.

The process according to the invention is

also suitable for the preparation of amorphous or rubber-like copolymers based on ethylene and another  $\alpha$ -olefin. Propylene is preferably used as the other  $\alpha$ -olefin so that EPM rubber is formed. It is also quite possible to use a diene in addition to ethylene and the other  $\alpha$ -olefin, so that a so-called EADM rubber is formed, in particular EPDM (ethylene propylene diene rubber).

The catalyst composition according to the invention can be used supported as well as non-supported. The supported catalysts are used mainly in gas phase and slurry processes. The carrier used may be any carrier known as carrier material for catalysts such as, for instance,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{MgCl}_2$ . These carriers can be used as such or modified, for example, by silanes and/or Al-alkyls and/or aluminoxane compounds, and the like. Preferably, the aluminoxane is a (modified) methyl aluminoxane.

Those skilled in the art will easily understand that the catalyst systems used in accordance with this invention may also be prepared by in situ methods.

Polymerization of the olefin can be effected in a known manner. For example, polymerization can be a solid phase powder polymerization, a gas phase polymerization using, for example, a fluidized bed reactor, or a polymerization carried out in a liquid reaction medium. If a liquid reaction medium is used, both solution and suspension polymerization are suitable. The quantity of transition metal to be used generally is such that its concentration in the dispersion agent can be between about  $10^{-8}$  mol/L and about  $10^{-3}$  mol/l, and preferably, between about  $10^{-7}$  mol/L and about  $10^{-4}$  mol/l.

The process according to the invention will hereafter be elucidated with reference to a

polyethylene preparation known per se, which is representative of the olefin polymerizations disclosed herein. For the preparation of other polymers on the basis of an olefin, the reader is expressly referred to  
5 the multitude of publications on this subject.

The preparation of polyethylene relates to a process for homopolymerization or copolymerization of ethylene with one or more  $\alpha$ -olefins having 3-12 carbon atoms and optionally one or more non-conjugated dienes.  
10 Suitable  $\alpha$ -olefins include propylene, butene, hexene, styrene, and octene. Suitable dienes include, for example, 1,7-octadiene, 1,9-decadiene, ethylidene norbornene, methylene norbornene, 1,5-cyclooctadiene, dicyclopentadiene, 1,4-hexadiene, and polyenes.

15 The process of the present invention can be conducted as a gas phase polymerization (e.g. in a fluidized bed reactor), solution or slurry/suspension polymerization or solid phase powder polymerization. For a gas phase polymerization, no solvents or  
20 dispersion media are required. For solution or slurry polymerization processes, a solvent or a combination of solvents may be employed if desired. Suitable solvents include toluene, ethylbenzene, one or more saturated, straight or branched aliphatic hydrocarbons, such as  
25 butanes, pentanes, hexanes, heptanes, pentamethyl heptane or mineral oil fractions such as light or regular petrol, naphtha, kerosine or gas oil. For polymerization under slurry conditions, a suspension utilizing a perfluorinated hydrocarbon or similar  
30 liquid may also be used.

In addition, excess olefinic monomer can be used as the reaction medium in a so-called bulk polymerization process.

Aromatic hydrocarbons can be used as solvent  
35 or dispersion medium, but because of their cost as well as on account of safety considerations, it will be



preferred not to use such solvents for production on a commercial scale. In polymerization processes on a commercial scale, it is preferred therefore to use as solvent the low-priced aliphatic hydrocarbons or mixtures thereof, as marketed by the petrochemical industry. If an aliphatic hydrocarbon is used as solvent, the solvent may yet contain minor quantities of aromatic hydrocarbon such as, for instance, toluene. Thus, if for instance methyl aluminoxane (MAO) is used as co-catalyst, toluene can be used as solvent for the MAO in order to supply the MAO in dissolved form to the polymerization reactor. Drying or purification of the solvents is desirable if such solvents are used. This can be done without problems by the average person skilled in the art.

In the process of the invention, the catalyst and the co-catalyst are used in a catalytically effective amount, i.e. any amounts that successfully results in the formation of polymer. Such amounts may be readily determined by one skilled in the art.

If a solution or bulk polymerization is used, it is preferably carried out at temperatures well above the melting point of the polymer to be produced. This is typically but not limited to temperatures between about 120°C and about 260°C. According to a preferred embodiment of the invention, the process is carried out under suspension or gas phase polymerization conditions which typically take place at temperatures well below the melting temperature of the polymer to be produced, typically, but not limited to, temperatures below 105°C.

The polymer solution or suspension resulting from the polymerization can be worked up by a method known per se. In general, the catalyst is de-activated at some point during the processing of the polymer. The de-activation is also effected in a manner known per se, e.g. by means of water or an alcohol. Removal

of the catalyst residues can be mostly omitted because the quantity of catalyst in the polymer, in particular the content of halogen and transition metal, is very low because of the use of the catalyst system according to the invention.

Polymerization can be effected at sub-atmospheric pressure, at atmospheric pressure or at an elevated pressure, and under conditions where at least one of the monomers is a liquid, which can be realized by application of suitable combinations of pressure and temperature e.g. bulk polymerization.

The process can be carried out continuously or discontinuously. If the polymerization is carried out under pressure, the yield of polymer can be increased substantially resulting in an even lower catalyst residue content. Polymerization can be performed at pressures between about 0.1 MPa and about 25 MPa. Higher pressures of 25 MPa and upwards can be applied if the polymerization is carried out in so-called high-pressure reactors. In such a high-pressure process, the catalyst according to the present invention can also be used with good results.

The polymerization can also be performed in several steps, in series, as well as in parallel. If required, the catalyst composition, temperature, hydrogen concentration, pressure, residence time, etc. can be varied from step to step. This conventional way to obtain products with a broad molecular weight distribution can also be applied to the process of the present invention. However, the catalysts used in the process of this invention produce resins with a molecular weight distribution that is in most cases (i.e. for most applications) broad enough for easy processing without the need of additional technical measures, i.e. without mixing of various catalysts or

several catalyst components and without the need for tandem reactors.

Because of the broad MWD the obtained polyolefins are very suitable for processing into a film, a blow-molded article, a rotational molded article, a cured article or a foam. The obtained polyolefins can also be functionalized.

The invention also relates to a polyolefin that can be obtained by means of a polymerization process with utilization of the catalyst composition according to the invention. The invention also relates to broad MWD polymer resins which can be obtained by means of the polymerization process according to the invention.

The invention will now be illustrated by means of the following non-limiting examples.

#### EXAMPLES

All experiments involving organometallic compounds were carried out with use of an inert nitrogen atmosphere using standard Schlenk equipment.

A method for the synthesis of (dimethylaminoethyl)-tetramethyl cyclopentadienyl was published by P. Jutzi et al., Synthesis, 684 (1993), which is hereby incorporated by reference.

$\text{TiCl}_3$ , the esters used and the lithium reagents, 2-bromo-2-butene and 1-chlorocyclohexene were obtained from Aldrich Chemical Company.  $\text{TiCl}_3 \cdot 3\text{THF}$  was obtained by heating  $\text{TiCl}_3$  for 24 hours in THF with reflux (THF is tetrahydrofuran).

The following abbreviations have been used: 'Me' means 'methyl'; 'iPr' means 'isopropyl'; 'Bu' means 'butyl'; 'iBu' means 'isobutyl'; 'tertBu' means 'tertiary butyl'; 'Ind' means 'indenyl'; 'Flu' means 'fluorenyl'; 'Ph' means 'phenyl';

Cp=cyclopentadienyl; and Cp\* = tetra methyl cyclopentadienyl.

Pressures refer to absolute pressures.

MWD is molecular weight distribution, defined  
5 as Mw/Mn. Unless stated otherwise Mz, Mw and Mn are molecular weights determined using universal calibration procedure in SEC-DV measurements.

#### General Polymerization Conditions

10 The following general polymerization conditions were used in the following examples unless otherwise indicated. Octene was first distilled and then dried over molecular sieves. 600 ml of an alkane solvent was introduced, under dry N<sub>2</sub>, into a 1.5 L  
15 stainless steel reactor. For the ethylene/octene copolymerization, 10 g dry octene was introduced into the reactor. The reactor was subsequently heated to the polymerization temperature of 80°C while stirring under an ethylene pressure of 8 bar (800 kPa).

20 In a catalyst premixing vessel with a volume of 100 Ml, 25 ml of an alkane solvent mixture was dosed, followed by 3 mmol of the co-catalyst methylaluminoxane (MAO obtained from Witco, 10% in toluene) and 1 micromol of the transition metal  
25 compound (Al/Ti-ratio 3,000): The co-catalyst and the transition metal compound were stirred for 1 minute before they were introduced into the reactor. The introduction of the cocatalyst/transition metal compound mixture into the reactor started the  
30 polymerization reaction. All polymerizations described were performed isothermally. The ethylene pressure was kept constant at 8 bar. After 7 minutes, the ethylene pressure was allowed to drop to zero, the reaction mixture was drained from the reactor and quenched with  
35 methanol. Antioxidant (Irganox 1076, TM) was added to

stabilize the polymer. Finally the polymer was dried under vacuum at 70°C for 24 hours.

Characterization data for the resultant polymers were obtained by NMR and SEC-DV methods.

5

Example I Preparation of an ethylene homopolymer with bimodal molecular weight distribution.

10 Synthesis of the [Cp(2,5-dimethyl-3,4-diethyl)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]TiCl<sub>2</sub> catalyst.

Ia. Preparation of 2,5-dimethyl-3,4-diethylcyclopentadienyldimethylaminoethyl

In a three neck roundbottom flask of 500 Ml 0.75 g (108 mmol), Li-wire was weighed. 150 mL dry  
15 diethylether was added. The solution was cooled to 0°C and in the next step 7.7 g (51.7 mmol) 2-bromo-2-pentene was added in a dropwise manner. The reaction that took place was exothermic. The reaction was completed at room temperature during 1 hour of  
20 stirring. Then, the solution was cooled to 0°C and 4 mL (25.3 mmol) ethyl-3-dimethylaminopropionate were added dropwise. Then, slowly 50 mL H<sub>2</sub>O was added. The water and ether layers were separated, and the water layer was extracted with 3 portions of 100 mL  
25 diethylether. The collected ether layers were dried on Na<sub>2</sub>SO<sub>4</sub>. After 1 hour of stirring, the Na<sub>2</sub>SO<sub>4</sub> was filtered off and the filtrate was dried by evaporation of the solvent. The residue was a yellow liquid. From NMR data, it was concluded that the carbinol had been  
30 synthesized. The yield was 5 grams (83%).

Then 8.44 g (44.4 mmol) paratoluenesulfonic acid monohydrate were dissolved in 200 ml diethylether. Then 5 g (20.9 mmol) of the carbinol was added. The solution turned a white/yellow color. The reaction  
35 mixture was stirred for 2.5 hours, and subsequently a

solution of  $\text{Na}_2\text{CO}_3$  in water was added. The water and ether layers were separated. The water layer was extracted with two portions of 50 mL ether. The collected ether layers were dried with  $\text{Na}_2\text{SO}_4$ . After 1  
5 hour of stirring, the  $\text{Na}_2\text{SO}_4$  was filtered off, and the solvent was evaporated from the filtrate. The residue was a yellow liquid. NMR-data showed that the residue was a mixture of carbinol and product. The yield was 3.58 g.

10 The 3.58 g of ligand were dissolved in 90 mL diethylether. The solution was cooled and 12 mL of a 1.6 M butyllithium solution in hexane were added. The reaction was completed while stirring during 2 hours at room temperature. Then, the solvent was evaporated.  
15 The residue was a yellow solid. The residue was washed several times with a C6-hydrocarbon and ether and was subsequently dried well. From NMR-data in perdeutero-THF, it appeared that the ligand-anion was pure. Yield: 0.85 g (15%).

20

Ib. Preparation of (dimethylaminoethyl)2,5-dimethyl-3,4-diethylcyclopentadienyltitanium(III)dichloride

In a Schlenk vessel, 0.76 g (3.347 mmol) ligand anion of Example IIa was dissolved in 40 mL THF.  
25 In a second Schlenk vessel, 1.20 g (3.238 mmol)  $\text{TiCl}_3 \cdot 3\text{THF}$  was slurried in 30 mL THF. Both Schlenk vessels were cooled to  $-60^\circ\text{C}$ , and then the anion was added to the  $\text{TiCl}_3$ . The solution was colored green. After 30 minutes, the cooling was stopped. The  
30 reaction was completed during stirring at room temperature for 1 hour. The solution was colored brown/green. Then, the solvent was evaporated. The residue was a green solid. The residue was slurried in 50 mL C6-hydrocarbon and dried again. The residue was a  
35 green/grey solid. The product was analyzed using mass

spectroscopy and was shown to be the desired complex.

#### Ic. Polymerization

Under the general polymerization conditions described above, an ethylene polymerization was performed with 5 micromol of the transition metal compound  $\text{Et}(\text{Cp}(2,5\text{-dimethyl-3,4-diethyl}))\text{NMe}_2\text{TiCl}_2$  at  $80^\circ\text{C}$ . This transition metal compound was mixed with 10 mmol MAO for 1 minute (Al/Ti ratio 2,000) and subsequently dosed to the reactor. After 7 minutes of polymerization, the reaction mixture was drained from the reactor. The polymer had an Mw of 235,000 g/mol, an Mz of 2,350,000 g/mol and a bimodal MWD of 30.

Example II Preparation of an ethylene/octene copolymer with bimodal molecular weight distribution.

Under the conditions described in example Ic, an ethylene/octene copolymerization was performed with the transition metal complex described in example Ib. 10 g of octene was added to the reactor. The copolymer formed had an Mw of 120,000 g/mol, an Mz of 910,000 g/mol, and a bimodal MWD of 14.6.

#### Example III

Synthesis of the (dimethylaminoethyl)tetramethylcyclopentadienyltitanium(III)dichloride catalyst.

##### III.a. Preparation of 4-hydroxy-4-(dimethylaminoethyl)-3,5-dimethyl-2,5-heptadiene

2-bromo-2-butene (108 g; 0.800 mol) was added to 10.0 g of lithium (1.43 mol) in diethyl ether (300 ml) in about 30 minutes with reflux. After stirring overnight (17 hours), ethyl-3-(N,N-dimethylamino)propionate (52.0 g; 0.359 mol) was added

- 30 -

to the reaction mixture in about 15 minutes. After stirring for 30 minutes at room temperature 200 ml of water was added dropwise. After separation the water phase was extracted two times with 50 ml of  $\text{CH}_2\text{Cl}_2$ . The organic phase was reduced by evaporation and the residue was distilled at reduced pressure. The yield was 51.0 g (67%).

10 III.b. Preparation of (dimethylaminoethyl)tetramethylcyclopentadiene

The compound (21.1 g; 0.10 mol) prepared as described under a) was added in a single portion to p-toluenesulphonic acid. $\text{H}_2\text{O}$  (28.5 g; 0.15 mol), dissolved in 200 ml of diethyl ether. After stirring for 30 minutes at room temperature the reaction mixture was poured out in a solution of 50 g of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  in 250 ml of water. After separation the water phase was extracted two times with 100 ml of diethyl ether. The combined ether layer was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and evaporated. Then the residue was distilled at reduced pressure. The yield was 11.6 g (60%).

25 III.c. Preparation of (dimethylaminoethyl)tetramethylcyclopentadienyltitanium(III)dichloride

1.0 equivalent of n-BuLi (1.43 ml; 1.6 M) was added (after cooling to  $-60^\circ\text{C}$ ) to a solution of the  $\text{C}_5\text{Me}_4\text{H}(\text{CH}_2)_2\text{NMe}_2$  of b) (0.442 g; 2.29 mmol) in THF (50 ml), after which the cooling bath was removed. After warming to room temperature the solution was cooled to  $-100^\circ\text{C}$  and then  $\text{TiCl}_3 \cdot 3\text{THF}$  (0.85 g; 2.3 mmol) was added in a single portion. After stirring for 2 hours at room temperature the THF was removed at reduced pressure. After addition of special boiling point gasoline the complex (a green solid) was purified by repeated washing of the solid, followed by filtration and



backdistillation of the solvent. It was also possible to obtain the pure complex through sublimation.

Example IV Preparation of an ethylene/octene copolymer with bimodal molecular weight distribution using a supported catalyst .

IVa. preparation of a supported catalyst

A supported catalyst was synthesized by adding 10 ml dry toluene to 1.453 g SiO<sub>2</sub> (Grace/Davison silica type W952, dried during 4 hours at 400°C under dry N<sub>2</sub>), followed by the addition, during 10 minutes under stirring at 300 K, of 16 ml MAO (Witco, 30% in toluene). This mixture was dried at room temperature while stirring under vacuum for 2 hours. Then 25 ml of a dry alkane mixture was added, and the slurry that was formed was stirred during 12 hours at 300 K. Then a suspension of the transition metal compound [Cp\*CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]<sub>2</sub>TiCl<sub>2</sub> was added while stirring at 300 K. After this mixture had been dried, the catalyst contained 27.9 wt% Al and an Al/Ti-ratio of 328.

IVb. Polymerization

Under the general polymerization conditions described above, a polymerization was performed with this supported catalyst. No additional MAO was used. 18 g octene was added to the reactor, followed by 20 micromol (based on Ti) of the supported catalyst. Then, the copolymerization was performed at 80°C at 8 bar ethylene. The polymer yield was determined to be 28,050 kg/mol Ti\*hour. The polymer was analyzed using SEC-DV. The Mw was determined to be 400,000 g/mol, the octene content of the copolymer was 9.9 wt.% (from <sup>1</sup>H-NMR). The polymer had a bimodal MWD determined with SEC-DV, of 15.

Example V Preparation of an ethylene homopolymer with bimodal molecular weight distribution using a supported catalyst .

5 Va. Preparation of supported catalyst

A supported catalyst was produced by introducing 2.646 g MAO/SiO<sub>2</sub> (Witco, containing 21.7 wt.% Al) in a Schlenk vessel. 20 ml dry alkane solvent (C<sub>6</sub>-fraction) was added at 300 K to form a slurry of  
10 the MAO/SiO<sub>2</sub> in the solvent. A solution of the transition metal complex [Cp\*CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]<sub>2</sub>TiCl<sub>2</sub> was added to the slurry; the mixture was dried under vacuum while stirring at 300 K. A free flowing powder was formed with an Al/Ti-ratio of 178.

15 1.0417 g of this catalyst powder was put in a Schlenk vessel, washed with 40 ml dry toluene at 300 K and subsequently dried under vacuum at 300 K during 20 minutes to form a free flowing powder.

20 Vb. Polymerization

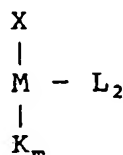
Using 5 micromol (on Ti-basis) of this catalyst powder, a polymerization reaction was performed as described in Example IV at 80°C. The ethylene pressure, however, was now 600 kPa. The  
25 ethylene homopolymer formed was studied with SEC-DV using conventional calibration. The polymer formed had an ultra high molecular weight ( $M_w = 1.35 \cdot 10^6$  g/mol) and had a bimodal MWD of 10.4.

Table 1  
Examples of transition metal complexes according to the invention (see formulas I and VI)

M	L	Y	R	D	R'	K
Ti	Cl	C <sub>5</sub> H <sub>6</sub>	dimethylsilyl	N	methyl	L
Zr	F	C <sub>5</sub> Me <sub>4</sub>	diethylsilyl	P	ethyl	Y-R'
Hf	Br	Indenyl	dipropylsilyl	As	propyl	X
V	I	Fluorenyl	dibutylsilyl	Sb	n-butyl	diethyl ether
Nb	methyl	benzofluorenyl	methylamido	O	n-pentyl	tetrahydrofuran
Ta	methoxy	octahydrofluorenyl	dimethylgermanyl	S	methoxy	trimethylamine
Cr	ethoxy	C <sub>5</sub> H <sub>3</sub> (N-Bu)	diethylgermanyl	Se	ethoxy	triethylamine
Mo	hydride	tetrahydroindenyl	diethylpropylene		Cl	trimethylphosphine
W	isopropyl octyl propoxy phenoxyl benzyl methylthio	C <sub>5</sub> H <sub>3</sub> (SiMe <sub>3</sub> ) methylamido phenylphosphido	tetramethyldisiloxane diphenylsilyl tetramethylsilaethylene methylene diethylmethylene ethylene dimethylethylene ethylphosphido phenylphosphido		F Br I phenoxyl benzyl H	triethylphosphine triphenylphosphine dimethylsulfide dimethylaniline

WHAT IS CLAIMED IS:

1. A process for preparing a polyolefin resin having at least a bimodal molecular weight distribution which comprises polymerizing one or more olefins in the presence of a catalyst comprising a reduced transition metal complex and a co-catalyst, wherein said reduced transition metal complex has the following structure:



wherein:

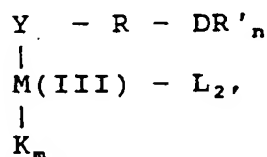
- M is a reduced transition metal selected from group 4, 5 or 6 of the Periodic Table of the Elements;
- X is a multidentate monoanionic ligand represented by the formula  $(\text{Ar}-\text{R}_t-)_q\text{Y}(-\text{R}_t-\text{DR}'_n)_q$ ;
- Y is a member selected from the group consisting of a cyclopentadienyl, amido  $(-\text{NR}'-)$ , and phosphido  $(-\text{PR}'-)$  group;
- R is at least one member selected from the group consisting of (i) a connecting group between the Y group and the  $\text{DR}'_n$  group and (ii) a connecting group between the Y group and the Ar group, wherein when the ligand X contains more than one R group, the R groups can be identical as or different from each other;
- D is an electron-donating hetero atom selected from group 15 or 16 of the Periodic Table of Elements;

- R' is a substituent selected from the group consisting of a hydrogen, hydrocarbon radical and hetero atom-containing moiety, except that R' cannot be hydrogen when R' is directly bonded to the electron-donating hetero atom D, wherein when the multidentate monoanionic ligand X contains more than one substituent R', the substituents R' can be identical or different from each other;
- Ar is an electron-donating aryl group;
- L is a monoanionic ligand bonded to the reduced transition metal M, wherein the monoanionic ligand L is not a ligand comprising a cyclopentadienyl, amido ( $-NR'-$ ), or phosphido ( $-PR'-$ ) group, and wherein the monoanionic ligands L can be identical or different from each other;
- K is a neutral or anionic ligand bonded to the reduced transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or different from each other;
- m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for  $M^{3+}$ , m is 1 for  $M^{4+}$ , and m is 2 for  $M^{5+}$ , and when K is a neutral ligand m increases by one for each neutral K ligand;
- n is the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from group 16 of the Periodic Table of Elements n is 1;
- q and s are the number of ( $-R_t-DR'_n$ ) groups and ( $Ar-R_t-$ ) groups bonded to group Y,

respectively, wherein  $q + s$  is an integer not less than 1; and

$t$  is the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and  $DR'_n$  groups, wherein  $t$  is selected independently as 0 or 1.

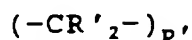
2. A process according to claim 1, wherein the Y group is a cyclopentadienyl group.
3. A process according to claim 2, wherein the cyclopentadienyl group is an unsubstituted or substituted indenyl, benzoindenyl, or fluorenyl group.
4. A process according to claim 2, wherein said reduced transition metal complex has the following structure:



wherein:

$M(III)$  is a transition metal from group 4 of the Periodic Table of the Elements in oxidation state 3+.

5. A process according to claim 2, wherein said reduced transition metal is titanium.
6. A process according to claim 2, wherein said electron-donating hetero atom D is nitrogen.
7. A process according to claim 2, wherein the  $R'$  group in the  $DR'_n$  group is an n-alkyl group.
8. A process according to claim 2, wherein said R group has the following structure:



wherein p is 1, 2, 3, or 4.

9. A process according to claim 2, wherein said monoanionic ligand L is selected from the group consisting of a halide, an alkyl group, and a benzyl group.
10. A process according to claim 2, wherein the Y group is a di-, tri- or tetraalkyl-cyclopentadienyl.
11. A process according to claim 2, wherein said co-catalyst comprises a linear or cyclic aluminoxane or a triaryl borane or tetraaryl borate.
12. A process according to claim 2, wherein at least one member selected from the group consisting of said reduced transition metal complex and said co-catalyst is supported on at least one carrier.
13. A process according to claim 1, wherein said polymerization is carried out at a temperature below about 160°C.
14. A process according to claim 1, wherein said olefin has been selected from the group consisting of  $\alpha$ -olefin, vinyl aromatic monomer, internal olefin, cyclic olefin, di-olefin, and mixtures thereof.
15. A process according to claim 1, wherein said olefin is selected from the group consisting of ethylene, propylene, butene, pentene, hexene, heptene, octene, styrene, and mixtures thereof.
16. A process according to claim 1, wherein said olefin is ethylene, propylene, or a mixture thereof.
17. A process according to claim 1, wherein said olefin is styrene, ethylene, or a mixture thereof.
18. A process according to claim 1, wherein said polyolefin resin is prepared by copolymerization of ethylene, an  $\alpha$ -olefin, and an optional diene.

19. A polyolefin resin prepared by a process according to claim 1.
20. A film formed from a polyolefin resin prepared by a process according to claim 1.
21. An article comprising a blow molded polyolefin resin prepared by a process according to claim 1.
22. An article comprising a polyolefin resin prepared by a process according to claim 1 and which is formed by rotation moulding.
23. An article comprising a cured form of a polyolefin resin prepared by a process according to claim 1.
24. A foam comprising a polyolefin resin prepared by a process according to claim 1.
25. A product comprising a functionalized form of the polyolefin resin prepared according to claim 1.



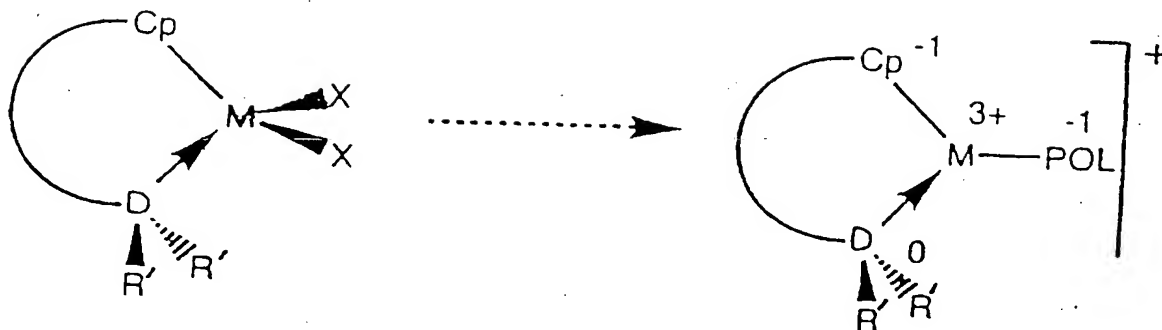


FIG. 1

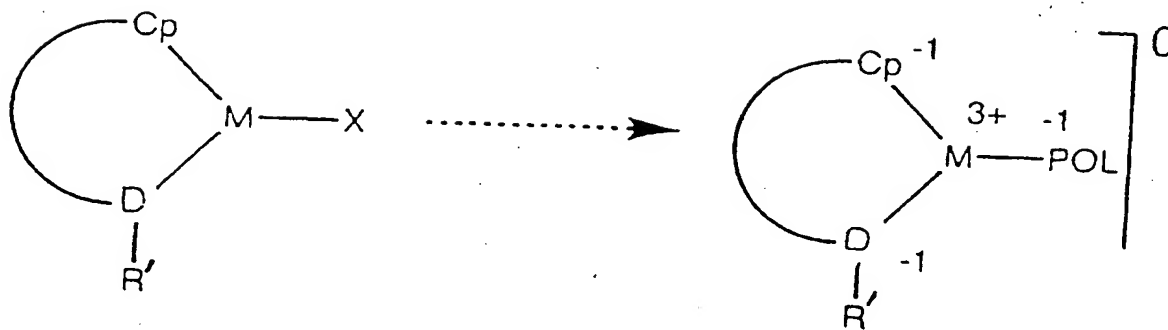


FIG. 2

# INTERNATIONAL SEARCH REPORT

Inter. Application No  
PCT/NL 97/00241

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F210/16 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 96 13529 A (DSM NV; BEEK JOHANNUS ANTONIUS MARIA V (NL); DOREMAELE GERARDUS HE) 9 May 1996 * claims; examples VII-LVI *	1-25
A	WO 93 08221 A (DOW CHEMICAL CO) 29 April 1993 * claims; page 41, table 1, example 1 *	1-25
X	EP 0 447 070 A (BP CHEM INT LTD; BP CHEMICALS SNC (FR)) 18 September 1991 cited in the application * page 7, lines 50 to 55; page 11, example 5 *	19-25

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 June 1997

Date of mailing of the international search report

26.06.97

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/NL 97/00241

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 619 325 A (FINA RESEARCH) 12 October 1994 cited in the application * claims; pages 9 and 10, table 2, examples 5 to 23 *	19-25

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Information on patent family members

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